

## Polymer Chemistry (SEM VI Honours)

**Syllabus:** Criteria for polymer solubility, Solubility parameter, Thermodynamics of polymer solutions, entropy, enthalpy, and free energy change of mixing of polymer solutions, Flory-Huggins theory, Lower and Upper critical solution temperatures.

### POLYMER SIZE AND SHAPE

The general problem of the size and shape of polymer molecules stands at the very heart of polymer science and engineering. If the molecular weight and molecular weight distribution (MWD) are known along with a good understanding of the polymer chain conformation, many mechanical and rheological properties can be predicted.

1. The molecular weights of polymers are very high, ranging from about 25,000 to 1,000,000 g/mol or higher. At lower molecular weights, the term *oligomer* is used for a polymer with only a few repeat units, having degrees of polymerization of not more than 10 to 100 (1). Assuming a molecular weight of 50 g/mol for each mer, a range of molecular weights of up to 500 to 5000 g/mol result. Although the term *telomer* is sometimes used for higher molecular weight materials, it is used primarily for polymers whose molecular weights are in the oligomer range. It refers especially to those materials formed by chain transfer reactions. The term *telechelic* polymers is used for oligomers and telomers with functional groups on both ends (2). Telechelic polymers are usually intended for further chemical reaction, particularly polymer network formation. Polymers having a reactive group at only one end are called *macromers* (3) (an abbreviation for *macromonomers*), and they are intended for further reaction. Super high molecular weight polymers with molecular weights greater than  $1 \times 10^7$  g/mol have been called *pleistomers* (3).

2. The molecular weight of ordinary size molecules is fixed (e.g., benzene has a molecular weight of 78 g/mol regardless of its source). Most polymer molecular weights, on the other hand, vary greatly depending on the method of preparation. In addition most polymers are polydisperse; that is, the sample contains more than one species.

3. The spatial arrangement of the polymer chain is called its "conformation." Conformations can be determined in dilute solutions by light scattering, and in the bulk state by small-angle neutron scattering (SANS). Conformations can also be estimated theoretically from the structure and molecular weight of the polymer.

4. Polymer chain conformations are functions of temperature, solvent, structure, crystallization, extension, and the presence of other polymers.

5. Another major problem in the polymer industry is that of rapid molecular weight determination.

### HOW DOES A POLYMER DISSOLVE?

Once placed in a solvent, polymers dissolve in several steps. First, the solvent must wet the polymer. Second, the solvent diffuses into the polymer, swelling it. For polymers of high molecular weight, this process may take several hours or longer, depending on sample size, temperature, and so on. Contrary to many low molecular weight substances, the polymer does not initially diffuse into the solvent.

There are two distinguishable modes of solvent diffusion into a polymer. If the polymer is amorphous and above its glass transition temperature (i.e., a polymer melt), the diffusion of the

solvent into the polymer forms a smooth composition curve, with the most highly swollen material at the outer edge. This is referred to as Fickian diffusion, following Fick's laws.

If the polymer is significantly below its glass transition temperature, however, the non-Fickian phenomenon known as case II swelling may predominate. In this situation the diffusion into the glassy polymer is slow. First the solvent must plasticize the polymer, lowering its glass transition temperature until it is below ambient. Then swelling is rapid. A rather sharp, moving boundary results between highly swollen material and that substantially not swollen. Frequently the stresses at the swelling boundary cause the sample to craze or fracture. A similar phenomenon is sometimes found with semicrystalline polymers.

Finally, the polymer diffuses out of the swollen mass into the solvent, completing the solution process. Very dilute solutions are usually required for molecular weight determination.

If the polymer is cross-linked, the polymer only swells, reaching an equilibrium degree of swelling. There are also some polymers, particularly with high melting temperatures or strong internal secondary bonds, that cannot be dissolved without degradation. In these last cases the polymer molecular weight cannot be determined directly, and sometimes not at all.

### THE SOLUBILITY PARAMETER

One of the simplest notions in chemistry is that "like dissolves like." Qualitatively, "like" may be defined variously in terms of similar chemical groups or similar polarities. Quantitatively, solubility of one component in another is governed by the familiar equation of the free energy of mixing,

$$\Delta G_M = \Delta H_M - T \Delta S_M \quad \dots\dots\dots(1)$$

where  $\Delta G_M$  is the change in Gibbs' free energy on mixing,  $T$  is the absolute temperature, and  $\Delta S_M$  is the entropy of mixing. A negative value of  $\Delta G_M$  indicates that the solution process will occur spontaneously. The term  $T\Delta S_M$  is always positive because there is an increase in the entropy on mixing. (But, note the negative sign!) Therefore, the sign of  $\Delta G_M$  depends on the magnitude of  $\Delta H_M$ , the enthalpy of mixing.

Surprisingly, the heat of mixing is usually positive, opposing mixing. This is true for big and little molecules alike. Exceptions occur most frequently when the two species in question attract one another in some way, perhaps by having opposite polarities, being acid and base relative to one another, or through hydrogen bonding. However, positive heats of mixing are the more usual case for relatively nonpolar organic compounds. On a quantitative basis, Hildebrand and Scott proposed that, for regular solutions,

$$\Delta H_M = V_M \left[ \left( \frac{\Delta E_1}{V_1} \right)^{1/2} - \left( \frac{\Delta E_2}{V_2} \right)^{1/2} \right]^2 v_1 v_2 \quad \dots\dots\dots(2)$$

where  $V_M$  represents the total volume of the mixture,  $\Delta E$  represents the energy of vaporization to a gas at zero pressure (i.e., at infinite separation of the molecules), and  $V$  is the molar volume of the components, for both species 1 and 2. The quantity  $v$  represents the volume fraction of component 1 or 2 in the mixture. The quantity  $\Delta E/V$  represents the energy of vaporization per

unit volume. This term is sometimes called the cohesive energy density. By convention, component 1 is the solvent, and component 2 is the polymer.

The reader should note that according to equation (2), “like dissolves like” means that the two terms  $\Delta E_1/V_1$  and  $\Delta E_2/V_2$  have nearly the same numerical values. Equation (2) also yields only positive values of  $\Delta H_M$ , a serious fault in the theory. However, since the majority of polymer solutions do have positive heats of mixing, the theory has found very considerable application.

The square root of the cohesive energy density is widely known as the solubility parameter,

$$\delta = \left( \frac{\Delta E}{V} \right)^{1/2} \dots\dots\dots(3)$$

Thus, the heat of mixing of two substances is dependent on  $(\delta_1 - \delta_2)^2$ . These relationships are meaningful only for positive heats of mixing; that is, when the heat of mixing term opposes solution. Since  $(\delta_1 - \delta_2)^2$  cannot be negative, equations (2) and (3) break down for negative heats of mixing.

### Solubility Parameter Tables

Tables 1 and 2 present the solubility parameters of common solvents and polymers, respectively. These tables provide a quantitative basis for understanding why methanol or water does not dissolve polybutadiene or polystyrene. However, benzene and toluene are predicted to be good solvents for these polymers, which they are. While solubility of a polymer also depends on its molecular weight, the temperature, and so on, it is frequently found that polymers will dissolve in solvents having solubility parameters within about one unit of their own, in  $(\text{cal}/\text{cm}^3)^{1/2}$ .

**Table 1 Solubility parameters of some common solvents**

Solvent	$\delta$		H-bonding <sup>a</sup> Group	Specific Gravity <sup>b</sup> 20°C (g/cm <sup>3</sup> )
	(cal/cm <sup>3</sup> ) <sup>1/2</sup>	MPa <sup>1/2</sup>		
Acetone	9.9	20.3	m	0.7899
Benzene	9.2	18.8	p	0.87865
n-Butyl acetate	8.5	17.4	m	0.8825
Carbon tetrachloride	8.6	17.6	p	1.5940
Cyclohexane	8.2	16.8	p	0.7785
n-Decane	6.6	13.5	p	—
Dibutyl amine	8.1	16.6	s	—
Difluorodichloromethane	5.5	11.3	p	—
1,4-Dioxane	7.9	16.2	m	1.0337
Low odor mineral spirits	6.9	14.1	p	—
Methanol	14.5	29.7	s	0.7914
Toluene	8.9	18.2	p	0.8669
Turpentine	8.1	16.6	p	—
Water	23.4	47.9	s	0.99823
Xylene	8.8	18.0	p	0.8611

Source: J. Brandrup, E. H. Immergut, and E. A. Grulke, eds., *Polymer Handbook*, 4th ed., Wiley-Interscience, New York, 1999.

<sup>a</sup>Hydrogen bonding is an important secondary parameter in predicting solubility. p, Poorly H-bonded; m, moderately H-bonded; and s, strongly H-bonded.

<sup>b</sup>J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3th ed., Wiley-Interscience, New York, 1989, sec. III, p. 29.

Note: 1 (cal/cm<sup>3</sup>)<sup>1/2</sup> = 2.046 × 10<sup>3</sup> (J/m<sup>3</sup>)<sup>1/2</sup>.

**Table 2 Solubility parameters and densities of common polymers**

Polymer	$\delta$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	$\delta$ (MPa) <sup>1/2</sup>	Density (g/cm <sup>3</sup> )
Polybutadiene	8.4	17.2	1.01
Polyethylene	7.9	16.2	0.85 (amorphous)
Poly(methyl methacrylate)	9.45	19.4	1.188
Polytetrafluorethylene	6.2	12.7	2.00 amorphous, estimated
Polyisobutene	7.85	16.5	0.917
Polystyrene	9.10	18.6	1.06
Cellulose triacetate (56% ac groups)	13.60	27.8	1.28 <sup>a</sup>
Cellulose tributyrate	—	—	1.16 <sup>a</sup>
Polyamide 66	13.6	22.9	1.24
Poly(ethylene oxide)	9.9	20.0	1.20
Poly(ethylene terephthalate), partly crystalline	10.7	21.9	1.38
Poly(ethylene terephthalate), amorphous	10.7	21.9	1.34
Poly(vinyl alcohol)	12.6	25.8	1.26
Poly(vinyl chloride)	9.6	19.8	1.39

Note: 1 (cal/cm<sup>3</sup>)<sup>1/2</sup> = 2.046 × 10<sup>3</sup> (J/m<sup>3</sup>)<sup>1/2</sup>.

<sup>a</sup> C. J. Malm, C. R. Fordyce, and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).

## THERMODYNAMICS OF MIXING

### Types of Solutions

**The Ideal Solution:** In the previous section the solubility of a polymer in a given solvent was examined on the basis of their respective solubility parameters, which was governed by the heats of mixing. The entropy of mixing was entirely ignored. In an ideal solution, the circumstances are reversed, and the heat of mixing is zero, by definition. Raoult's law is obeyed

$$p_1 = p_1^\circ n_1 \quad \dots\dots\dots(4)$$

where  $p_1$  is the partial vapor pressure,  $n_1$  is the mole fraction of component 1, and  $p_1^\circ$  is the vapor pressure of the pure component.

The free energy of mixing is given as the sum of the free energies of dilution per molecule, incompressibility of the mixture implicitly assumed:

$$\Delta G_M = N_1 \Delta G_1 + N_2 \Delta G_2 \quad \dots\dots\dots(5)$$

$$\Delta G_M = kT \left[ N_1 \ln \left( \frac{p_1}{p_1^\circ} \right) + N_2 \ln \left( \frac{p_2}{p_2^\circ} \right) \right] \quad \dots\dots\dots(6)$$

where  $N_1$  and  $N_2$  are the numbers of molecules of the 1 and 2 species, respectively. Then, from equation (4), for small molecules,

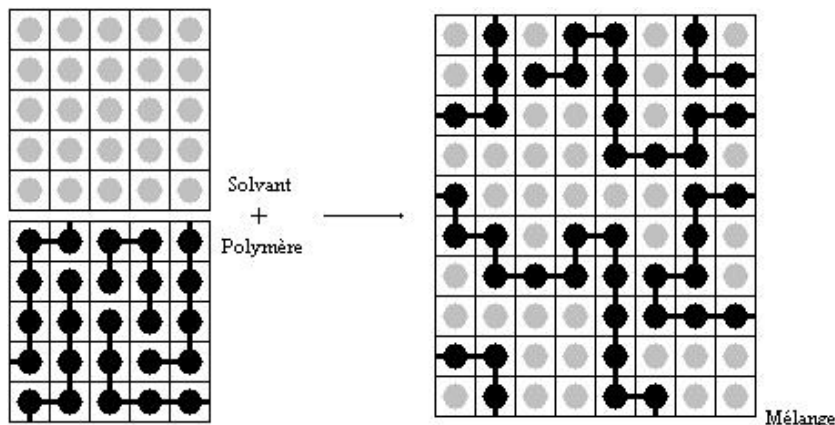
$$\text{Since } \Delta H_M = 0, \quad \Delta G_M = kT(N_1 \ln n_1 + N_2 \ln n_2) \quad \dots\dots\dots(7)$$

Since the entropy of mixing is always positive, and the heat of mixing is zero for an ideal solution, mixing in all proportions always occurs spontaneously.

$$\Delta S_M = -k(N_1 \ln n_1 + N_2 \ln n_2) \quad \dots\dots\dots(8)$$

## FLORY–HUGGINS SOLUTION THEORY

**Flory–Huggins solution theory** is a lattice model of the thermodynamics of polymer solutions which takes account of the great dissimilarity in molecular sizes in adapting the usual expression for the entropy of mixing. The result is an equation for the Gibbs free energy change  $\Delta G_m$  for mixing a polymer with a solvent. Although it makes simplifying assumptions, it generates useful results for interpreting experiments.



### Theory

The thermodynamic equation for the Gibbs energy change accompanying mixing at constant temperature and (external) pressure is

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

A change, denoted by  $\Delta$ , is the value of a variable for a solution or mixture minus the values for the pure components considered separately. The objective is to find explicit formulas for  $\Delta H_m$  and  $\Delta S_m$ , the enthalpy and entropy increments associated with the mixing process.

The result obtained by Flory and Huggins is

$$\Delta G_m = RT [ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} ]$$

or

$$\Delta G_M = kT ( N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2 )$$

The right-hand side is a function of the number of moles  $n_1$  and volume fraction  $\phi_1$  of solvent (component 1), the number of moles  $n_2$  and volume fraction  $\phi_2$  of polymer (component 2), with the introduction of a parameter  $\chi$  to take account of the energy of interdispersing polymer and solvent molecules.  $R$  is the gas constant and  $T$  is the absolute temperature. The volume fraction is analogous to the mole fraction, but is weighted to take account of the relative sizes of the molecules. For a small solute, the mole fractions would appear instead, and this modification is the innovation due to Flory and Huggins. In the most general case the mixing parameter,  $\chi$ , is a free energy parameter, thus including an entropic component. or

The first two terms of equation are entropic, while the last term on the right is enthalpic. Again, incompressibility is assumed, meaning that the free volume in the system is constant. The

equation provides a starting point for many equations of interest. The partial molar free energy of mixing may be written, after multiplying by Avogadro's number,

## Derivation

We first calculate the *entropy* of mixing, the increase in the uncertainty about the locations of the molecules when they are interspersed. In the pure condensed phases — solvent and polymer — everywhere we look we find a molecule. Of course, any notion of "finding" a molecule in a given location is a thought experiment since we can't actually examine spatial locations the size of molecules. The expression for the entropy of mixing of small molecules in terms of mole fractions is no longer reasonable when the solute is a macromolecular chain. We take account of this dissymmetry in molecular sizes by assuming that individual polymer segments and individual solvent molecules occupy sites on a lattice. Each site is occupied by exactly one molecule of the solvent or by one monomer of the polymer chain, so the total number of sites is

$$N = N_1 + xN_2$$

$N_1$  is the number of solvent molecules and  $N_2$  is the number of polymer molecules, each of which has  $x$  segments. For a random walk on a lattice we can calculate the entropy change (the increase in spatial uncertainty) as a result of mixing solute and solvent.

$$\Delta S_m = -k[ N_1 \ln(N_1/N) + N_2 \ln(xN_2/N) ]$$

where  $k$  is Boltzmann's constant. Define the lattice *volume fractions*  $\Phi_1$  and  $\Phi_2$

$$\begin{aligned}\phi_1 &= N_1/N \\ \phi_2 &= xN_2/N\end{aligned}$$

These are also the probabilities that a given lattice site, chosen at random, is occupied by a solvent molecule or a polymer segment, respectively. Thus

$$\Delta S_m = -k[ N_1 \ln \phi_1 + N_2 \ln \phi_2 ]$$

For a small solute whose molecules occupy just one lattice site,  $x$  equals one, the volume fractions reduce to molecular or mole fractions, and we recover the usual entropy of mixing.

In addition to the entropic effect, we can expect an *enthalpy* change. There are three molecular interactions to consider: solvent-solvent  $w_{11}$ , monomer-monomer  $w_{22}$  (not the covalent bonding, but between different chain sections), and monomer-solvent  $w_{12}$ . Each of the last occurs at the expense of the average of the other two, so the energy increment per monomer-solvent contact is

$$\Delta w = w_{12} - \frac{1}{2} (w_{22} + w_{11})$$

The total number of such contacts is  $xN_2 z \phi_1 = N_1 \phi_2 z$

Where  $z$  is the coordination number, the number of nearest neighbours for a lattice site, each one occupied either by one chain segment or a solvent molecule. That is,  $xN_2$  is the total number

of polymer segments (monomers) in the solution, so  $xN_2z$  is the number of nearest-neighbour sites to *all* the polymer segments. Multiplying by the probability  $\Phi_1$  that any such site is occupied by a solvent molecule, we obtain the total number of polymer-solvent molecular interactions. An approximation following mean field theory is made by following this procedure, thereby reducing the complex problem of many interactions to a simpler problem of one interaction.

The enthalpy change is equal to the energy change per polymer monomer-solvent interaction multiplied by the number of such interactions

$$\Delta H_m = N_1 \phi_2 z \Delta w$$

The polymer-solvent interaction parameter *chi* is defined as

$$\chi_{12} = z \Delta w / kT$$

It depends on the nature of both the solvent and the solute, and is the only *material-specific* parameter in the model. The enthalpy change becomes

$$\Delta H_m = kT N_1 \phi_2 \chi_{12}$$

Assembling terms, the total free energy change is

$$\Delta G_m = RT [ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} ]$$

where we have converted the expression from molecules  $N_1$  and  $N_2$  to moles  $n_1$  and  $n_2$  by transferring Avogadro's number  $N_A$  to the gas constant  $R = k N_A$ .

The value of the interaction parameter can be estimated from the Hildebrand solubility parameters  $\delta_a$  and  $\delta_b$

$$\chi_{12} = V_{seg} (\delta_a - \delta_b)^2 / RT$$

where  $V_{seg}$  is the actual volume of a polymer segment.

In the most general case the interaction  $\Delta w$  and the ensuing mixing parameter,  $\chi$ , is a free energy parameter, thus including an entropic component. This means that aside to the regular mixing entropy there is another entropic contribution from the interaction between solvent and monomer. This contribution is sometimes very important in order to make quantitative predictions of thermodynamic properties.

#### VALUES FOR THE FLORY–HUGGINS $\chi_1$ PARAMETER

The Flory–Huggins  $\chi_1$  parameter has been one of the most widely used quantities, characterizing a variety of polymer–solvent and polymer–polymer interactions. It is a unitless number. **Sometimes the Flory–Huggins parameter is written  $\chi_{1,2}$ , and sometimes just plain  $\chi$ .** While the original theory proposed that  $\chi_1$  be concentration independent, many polymer-solvent systems exhibits increases of  $\chi_1$  with polymer concentration. In that case the analytical representation of the experimentally found concentration dependence can be written as a power

series,  $\chi_1 = \chi^0 + \chi^1 v_2 + \chi^2 v_2^2$  where  $\chi^0$ ,  $\chi^1$ , and  $\chi^2$  are determined experimentally.

However, for many simple calculations, it is valuable to have a single number parameter. Typical values of  $\chi_1$  are illustrated in Table 3, where values were selected at low concentrations of polymer. If the value of  $\chi_1$  is below 0.5, the polymer should be soluble if amorphous and linear. When  $\chi_1$  equals 0.5, as in the case of the polystyrene–cyclohexane system at 34°C in Table 3, then the Flory  $\theta$  conditions exist. If the polymer is crystalline, as in the case of polyethylene, it must be heated to near its melting temperature, so that the total free energy of melting plus dissolving is negative. For very many nonpolar polymer–solvent systems,  $\chi_1$  is in the range of 0.3 to 0.4.

**Table 3 Flory–Huggins  $\chi_1$  values**

Polymer	Solvent	$T, ^\circ\text{C}$	$\chi_1$
Polystyrene	Toluene	25	0.37
Polystyrene	Cyclohexane	34	0.50
Polyisoprene	Benzene	25	0.40
Cellulose nitrate	Acetone	20	0.14
Cellulose nitrate	<i>n</i> -Propylacetate	20	−0.38
Poly(ethylene oxide)	Benzene	70	0.19
Poly(dimethyl siloxane)	Toluene	20	0.45
Polyethylene	<i>n</i> -Heptane	109	0.29
Poly(butadiene– <i>stat</i> –styrene)	Toluene	25	0.39
Poly(ethylene oxide)	Water	25	0.4 <sup>a</sup>

Source: J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1989, sec. VII, pp. 176–178.

<sup>a</sup>CRC *Handbook of Polymer–Liquid Interaction Parameters and Solubility Parameters*, Part II, p. 178 (major entries).

The starting point is equation  $\Delta G_M = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2)$

The basis usually taken is 1 cm<sup>3</sup>. The number of molecules of each species needs to be calculated for  $v_1 = 0.90$  and  $v_2 = 0.10$ . Densities are shown in Tables 1 and 2. For cyclohexane, C<sub>6</sub>H<sub>12</sub>, the molecular weight is 84 g/mol and the molar volume is (84 g/mol)/(0.7785 g/cm<sup>3</sup>)  $\approx$  108 cm<sup>3</sup>/mol. For 0.90 cm<sup>3</sup>, there are 0.0083 mol, or, using Avogadro’s number, 5.02 X 10<sup>21</sup> molecules,  $N_1$ . The density of polystyrene is 1.06 g/cm<sup>3</sup>, yielding a molar volume of 9.43 X 10<sup>3</sup> cm<sup>3</sup>/mol for a molecular weight of 10,000 g/mol, and for 0.10 cm<sup>3</sup>, 1.06 X 10<sup>−5</sup> mol of polystyrene, or 6.38 X 10<sup>18</sup> molecules,  $N_2$ . The value of  $\chi_1$  is 0.50, taken from Table 3. The free energy of mixing is given by

$$\begin{aligned} \Delta G_M &= 1.38 \times 10^{-23} \text{ J/K} \times 307 \text{ K} \\ &\quad \times (5.02 \times 10^{21} \ln 0.09 + 6.38 \times 10^{18} \ln 0.10 + 0.50 \times 5.02 \times 10^{21} \times 0.10) \\ \Delta G_M &= -1.24 \text{ J} \end{aligned}$$

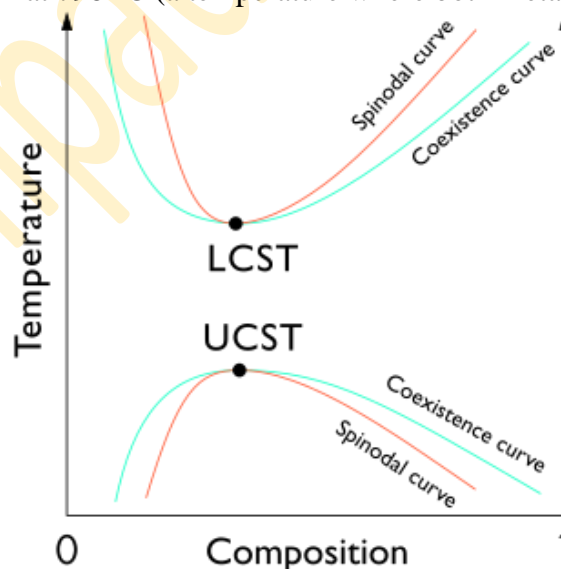
for each cm<sup>3</sup> of solution. The value of  $\Delta G_M$  is small and negative because of the entropy of mixing term.

## LOWER AND UPPER CRITICAL SOLUTION TEMPERATURE

The phase behaviour of polymer solutions is an important property involved in the development and design of most polymer-related processes. Partially miscible polymer solutions often exhibit two solubility boundaries, the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST), which both depend on the molar mass and the pressure. At temperatures below LCST, the system is completely miscible in all proportions, whereas above LCST partial liquid miscibility occurs.

The **lower critical solution temperature (LCST)** or **lower consolute temperature** is the critical temperature below which the components of a mixture are miscible for all compositions. The word *lower* indicates that the LCST is a lower bound to a temperature interval of partial miscibility, or miscibility for certain compositions only. For example, the system triethylamine-water has an LCST of 19 °C, so that these two substances are miscible in all proportions below 19 °C but not at higher temperatures. The nicotine-water system has an LCST of 61 °C, and also a UCST of 210°C at pressures high enough for liquid water to exist at that temperature. The components are therefore miscible in all proportions below 61 °C and above 210 °C (at high pressure), and partially miscible in the interval from 61 to 210 °C.

The **upper critical solution temperature (UCST)** or **upper consolute temperature** is the critical temperature above which the components of a mixture are miscible in all proportions. The word *upper* indicates that the UCST is an upper bound to a temperature range of partial miscibility, or miscibility for certain compositions only. For example, hexane-nitrobenzene mixtures have a UCST of 19 °C, so that these two substances are miscible in all proportions above 19 °C but not at lower temperatures. Examples at higher temperatures are the aniline-water system at 168 °C (at pressures high enough for liquid water to exist at that temperature), and the lead-zinc system at 798 °C (a temperature where both metals are liquid).



*A plot of typical polymer binary solution phase behaviour including both an LCST and a UCST*

In the phase diagram of the mixture components, the LCST is the shared minimum of the concave up spinodal and binodal (or coexistence) curves. It is in general pressure dependent, increasing as a function of increased pressure.

In the phase diagram of the mixture components, the UCST is the shared maximum of the concave down spinodal and binodal (or coexistence) curves. The UCST is in general dependent on pressure. The phase separation at the UCST is in general driven by unfavourable energetics; in particular, interactions between components favour a partially demixed state.

## Polymer-solvent mixtures

Some polymer solutions also have a lower critical solution temperature (LCST) or lower bound to a temperature range of partial miscibility. As shown in the diagram, for polymer solutions the LCST is higher than the UCST, so that there is a temperature interval of complete miscibility, with partial miscibility at both higher and lower temperatures. The UCST and LCST of polymer mixtures in general depend on polymer degree of polymerization, polydispersity, branching as well as on the polymer's composition and architecture. The seminal statistical mechanical model for the UCST of polymers is the Flory–Huggins solution theory. By adding soluble impurities, the upper critical solution temperature increases and lower critical solution temperature decreases.

A prominent polymer possessing an LCST is Poly(N-isopropylacrylamide) in water, which undergoes a reversible collapse transition related to the LCST at 33 °C. Another monomer whose homo- and copolymers exhibit LCST behaviour in solution is 2-(dimethylamino)ethyl methacrylate. The LCST depends on the polymer preparation and in the case of copolymers, the monomer ratios, as well as the hydrophobic or hydrophilic nature of the polymer.

## Physical basis

A key physical factor which distinguishes the LCST from other mixture behaviour is that the LCST phase separation is driven by unfavourable entropy of mixing. Since mixing of the two phases is spontaneous below the LCST and not above, the Gibbs free energy change ( $\Delta G$ ) for the mixing of these two phases is negative below the LCST and positive above, and the entropy change  $\Delta S = - (d\Delta G/dT)$  is negative for this mixing process. This is in contrast to the more common and intuitive case in which entropies drive mixing due to the increased volume accessible to each component upon mixing.

In general, the unfavourable entropy of mixing responsible for the LCST has one of two physical origins. The first is associating interactions between the two components such as strong polar interactions or hydrogen bonds, which prevent random mixing. For example, in the triethylamine water system, the amine molecules cannot form hydrogen bonds with each other but only with water molecules, so in solution they remain associated to water molecules with loss of entropy. The mixing which occurs below 19 °C is due not to entropy but to the enthalpy of formation of the hydrogen bonds. The second physical factor which can lead to an LCST is compressibility effects, especially in polymer-solvent systems. For nonpolar systems such as polystyrene in cyclohexane, phase separation has been observed in sealed tubes (at high pressure) at temperatures approaching the liquid-vapor critical point of the solvent. At such temperatures the solvent expands much more rapidly than the polymer, whose segments are covalently linked. Mixing therefore requires contraction of the solvent for compatibility of the polymer, resulting in a loss of entropy.

**Reference Book:** 1. L.H. Sperling, Introduction to physical polymer science, Fourth Edition, 2005, a John Wiley & Sons, Inc. Publication.

### Acknowledgement:

*The material has been developed with the help of different text books, journal material, Wikipedia and web help.*